

ADVANCED INORGANIC CHEMISTRY

A Comprehensive Text

F. ALBERT COTTON

ROBERT A. WELCH DISTINGUISHED PROFESSOR OF CHEMISTRY
TEXAS A AND M UNIVERSITY
COLLEGE STATION, TEXAS, USA

and

GEOFFREY WILKINSON

SIR EDWARD FRANKLAND PROFESSOR OF INORGANIC CHEMISTRY
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY
UNIVERSITY OF LONDON, ENGLAND

Fourth Edition, completely revised from the original literature

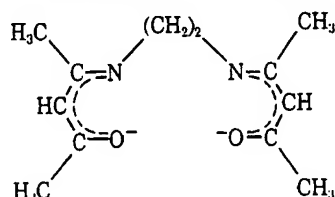
A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

NEW YORK • CHICHESTER • BRISBANE • TORONTO

BEST AVAILABLE COPY

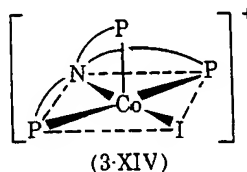
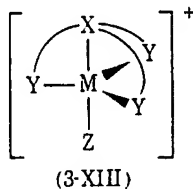
Schiff bases derived from acetylacetone, for example,



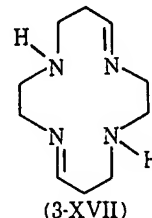
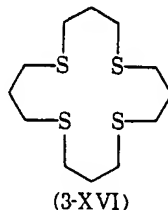
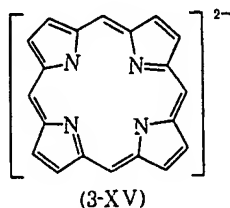
Tripod Ligands. These are of the type $X(Y)_3$, where X is nitrogen, phosphorus, or arsenic, the Y groups are R_2N , R_2P , R_2As , RS , or RSe , and the connecting chains— are $(CH_2)_2$, $(CH_2)_3$, or *o*-phenylene. Some common ones are

$N(CH_2CH_2NH_2)_3$	tren
$N[CH_2CH_2N(CH_3)_2]_3$	Me ₆ tren
$N[CH_2CH_2P(C_6H_5)_2]_3$	np ₃
$P[o-C_6H_4P(C_6H_5)_2]_3$	QP
$N(CH_2CH_2SCH_3)_3$	TSN
$As[o-C_6H_4As(C_6H_5)_2]_3$	QAS

The tripod ligands are used particularly to favor formation of trigonal-bipyramidal complexes of divalent metal ions, as shown schematically in 3-XIII, but they do not invariably give this result. For instance, whereas $Ni(np_3)I_2$ is trigonal-bipyramidal, $Co(np_3)I_2$ is square pyramidal (3-XIV).

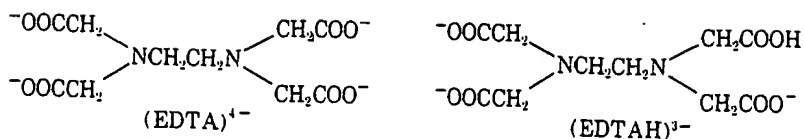


Macrocyclic. These may be (a) planar with unsaturated rings as in porphyrin (3-XV) and its derivatives, although, as discussed later in more detail (Section 4-14) the metal atom may be out of the plane of the nitrogen donor atoms, or (b) puckered with saturated rings as in the macrocycles 3-XVI and 3-XVII.

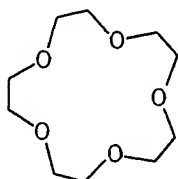


Pentadentate and Higher-Dentate Ligands. Perhaps the best known hexadentate ligand is ethylenediaminetetraacetate ($EDTA^{4-}$), which can also be pentadentate as $EDTAH^{3-}$.

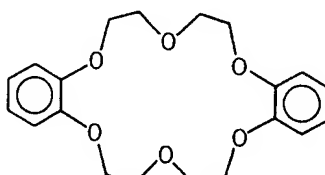
Other important multidentate ligands are the *crown ethers* and *cryptates*



portant complexes with alkali and alkaline earth ions. The macrocyclic polyethers, commonly called *crown ethers*, are typified by 3-XVIII and 3-XIX. Since the systematic names for such ligands are very unwieldy, a special nomenclature is used, in which 3-XVIII and 3-XIX are called, respectively, 15-crown-5 and dibenzo-18-crown-6. These examples should serve to show the rules for the simple nomenclature. Crown ethers with as many as ten oxygens are known and several (e.g., 3-XIX) are commercially available.

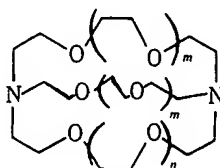


(3-XVIII)



(3-XIX)

The cryptates are bicyclic species, most of which have the general formula 3-XX. Again a simplified code for naming them is a practical necessity. They are called "cryptate-*mmn*," where *m* and *n* are as defined in 3-XX. One of the commonest is cryptate-222.



(3-XX)

These ligands have two characteristics that make them unusually interesting. Because they are chelating ligands of high denticity they give very high formation constants, and since the size of ion that will best fit the cavities can be predetermined by changing the ring size, these ligands can be designed to be selective.

In addition to the cryptates, which are synthesized apart from metal ions and then used to form complexes, there are other types of multicyclic ligand called *encapsulating ligands*, which are synthesized around the metal ion and cannot release it.⁹ Two of these are 3-XXI and 3-XXII. An encapsulation complex allows studies to be carried out under extremely acidic or basic conditions since the metal ion, though it cannot be removed, can be oxidized or reduced. Such ligands also can enforce unusual coordination geometries; in the examples shown the coordination is much closer to trigonal prismatic than to octahedral.

⁹ D. R. Boston and N. J. Rose, *J. Am. Chem. Soc.* 1973, 95, 1152-15.